AD

CCL REPORT NO. 294

FINAL REPORT
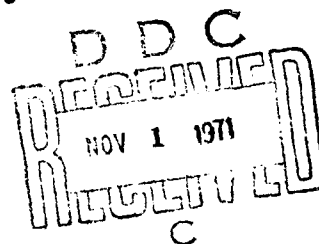
OXIDATION OF MERCAPTOBENZOTHIAZOLE TO

BENZOTHIAZYL DISULFIDE IN COOLANT MEDIA

BY

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JULES B. COUNTS

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U. S. ARMY
ABERDEEN RESEARCH & DEVELOPMENT CENTER
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13. ABSTRACT

Higher concentrations of mercaptobenzothiazole (MBT) are required in coolants to inhibit corrosion of metals in cooling systems of higher horsepower engines against corrosion. Since thiols such as MBT are easily oxidized, the mechanism of this reaction and the contributing factors of light, oxygen, and heat are evaluated. It is demonstrated that MBT is readily oxidized to the less soluble, terminal molecule of benzothiazyl disulfide by way of free radicals, and that this conversion is irreversible in coolant media. The possibility of deleterious operational effect of this conversion is considered.

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DEPARTMENT OF THE ARMY PROJECT NO.
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ABSTRACT

Higher concentrations of mercaptobenzothiazole (MBT) are required
in coolants to inhibit corrosion of metals in cooling systems of higher
horsepower engines against corrosion. Since thiols such as MBT are
easily oxidized, the mechanism of this reaction and the contributing
factors of light, oxygen, and heat are evaluated. It is demonstrated
that MBT is readily oxidized to the less soluble, terminal molecule of
benzothiazyl disulfide by way of free radicals, and that this conversion
is irreversible in coolant media. The possibility of deleterious
operational effect of this conversion is considered.

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I. INTRODUCTION

With the automotive industry's trend toward higher horsepower engines which produce more heat and the increased use of aluminum components in the automotive cooling system, it was found that increased amounts of mercaptobenzothiazole (MBT) were often required for adequate cooling system corrosion protection (Ref. 12). The corrosion inhibitor conforming to Federal Specification O-I-490 was modified recently to reflect this need and was designated as O-I-490a. This modification incorporated an increase in the amount of MBT, and phosphate was added.

During bench test evaluations with various antifreeze mixtures (Ref. 12) and the recommended amounts of O-I-490a corrosion inhibitor, it was observed that larger amounts of sediment were formed in the tests using O-I-490a than in the tests involving O-I-490. Infrared analysis showed the sediment to be essentially benzothiazyl disulfide (BTD). Accordingly, it was deemed necessary to determine if this conversion altered the effectiveness of MBT as a corrosion inhibitor in coolant formulations and to elucidate the mechanism of this reaction.

Work on this project was carried out under AMCMS Code 5025.11.803 dated 22 September 1967.

II. DETAILS OF TEST

A. Antifreeze Test Solutions. All test solutions were prepared in accordance with ASTM Method D-1176. The corrosion inhibitor conforming to Federal Specification O-I-490a was added at the rate of 1 ounce to 2 quarts of water present in the solutions. Comparable solutions were formulated substituting benzothiazyl disulfide (BTD) for MBT on an equal weight basis.

B. Glassware Corrosion Tests. Glassware corrosion tests were carried out in duplicate in accordance with ASTM Method D-1384, "Glassware Corrosion Test for Engine Antifreeze". To check the effect of light, heat and oxygen: one set of test beakers were painted with OD paint; the flow of air was replaced with a stream of commercial nitrogen in the second set; and the third set was run at room temperature (77°F.) rather than 180°F.

C. Numerical Rating Systems. A numerical rating system was used for purposes of comparing the various antifreeze solutions (see Table I). A rating of 10 or less was considered satisfactory. The arbitrary value was based on results determined on previously tested antifreezes which performed satisfactorily in the field.

D. Analysis of BTD.

1. Analysis of Residue. At the end of the glassware corrosion test, the solution was refrigerated for 48 hours. The sediment was

filtered, washed and air dried for two hours on a sintered glass filter.
The sediment was weighed and incorporated into a potassium bromide disc
of 0.025 mm. thickness, according to the Perkin Elmer Procedure (Ref. 13).
The amount of BTD was determined from the spectra of known mixtures of
MBT and BTD using the base line technique. The base line technique is
described in CCL Report No. 79 dated 5 August 1955 and Reference No. 18.
The base line was drawn from 6.09 to 6.27 microns. The "T" values were
obtained by measuring the difference from the 6.23 micron band maximum to
the base line intersection. A working curve was made by plotting the "T"
values of known MBT and BTD mixtures versus percent MBT (see Figure VI,
Appendix B).

     2. Analysis of BTD from Solution. At the end of the glassware
corrosion test the solution was extracted with chloroform and the com-
bined extracts dried over sodium sulfate. The dried solution was placed
in a 250 ml. volumetric flask and made up to volume. An aliquot was
taken from the volumetric flask and the BTD content determined on a
Beckman Ultra Violet Spectrophotometer Model DK-2A at 290 nm.

    E. Exposure of Dry MBT to Ultra Violet Light.

     1. A ten gram sample was taken from a freshly opened amber
colored bottle of MBT and spread into a uniform layer on a six inch watch
glass. The watch glass was placed on a window sill located at a southern
exposure for 28 days.

     2. A second sample was placed 12 inches from the direct rays
of a 6 Watt (standard white) ultra violet tube for 28 days.

     3. A ten gram sample was placed in a 50 ml. round bottomed
quartz flask, sealed and placed in an Atlas Ultra Violet Weatherometer
(Model DMC) for 28 days.

     4. The test in paragraph E3 was repeated except that the air
from the flask was evacuated and the flask was blanketed with nitrogen.

     5. At the end of the test periods, potassium bromide pellets
were made of the exposed samples and a fresh sample, according to the
Perkin Elmer Procedure (Ref. 13). Infrared spectra in the 2-15 micron
region were obtained of the resultant pellets using a Perkin Elmer Infra-
chord Spectrophotometer.

     6. Samples were also dissolved in chloroform and a melting point
and infrared spectrum was obtained of the insoluble portion.

III. RESULTS AND DISCUSSION

    A. Glassware Corrosion Tests. Tests were carried out with the
following solutions: (1) 30% O-A-548a/70% H O, (2) Arctic antifreeze
conforming to Military Specification MIL-A-11755B, and (3) 100% distilled
water. To each solution O-I-490a corrosion inhibitor was added at the

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rate of 1 ounce per 2 quarts of water present in the solution. Tables II, III and IV contain the results of tests carried out in glassware that had been apinted with OD paint so as to exclude the light. Tables V, VI and VII contain the results of tests carried out in clear glassware. Columns A and B of these tables contain the results of duplicate tests to which MBT had been added and columns C and D of these tables contain the results of tests to which BTD had been added. Table VIII contains a summary of the corrosion ratings (Table I). From the averages it will be seen that the corrosion ratings of tests in the painted glassware were slightly lower (i.e., superior). The combined average of the MBT tests was 8.6 and that of the BTD tests was 8.7. The difference is within the experimental limit of error of the method and shows that the inhibitor effectiveness of MBT and BTD are comparable.

Table IX contains a summary of the sediment values. The amounts of sediment in the tests substituting BTD for MBT were approximately threefold greater than those using MBT. This is to be expected because of the lower solubility of BTD in the test media. The exclusion of light reduced the amount of sediment, but the results show that air and heat also contribute to the oxidation of MBT. Infrared analysis of the residues showed them to be essentially BTD. Those from the MBT tests were approximately 75% BTD; those from the BTD tests were approximately 85% BTD. The results were obtained by the infrared base line technique using the 6.23 micron band of MBT (Fig. I, Appendix B). This band disappears entirely in a sample of pure BTD (Fig. IV). The 75% BTD and 85% BTD curves are shown in Figures II and III, respectively.

B. The contributory effect of oxygen in the conversion of MBT to BTD was evaluated by replacing the air in the glassware corrosion test with a stream of nitrogen. Parallel tests were carried out with air and nitrogen both in the light and dark colored bottles. These tests were repeated at room temperature (77°F.) in order to evaluate the contribution of heat to the oxidation process. The results of these tests are listed in Table X. It can be seen from these results that oxygen is an important factor in the conversion of MBT to BTD. It should be mentioned that the presence of oxygen is probably more pronounced than is reflected in the averages of 27.1% and 15.4%, since there is a certain amount of dissolved air in the solution and in the tank of nitrogen; so the nitrogen tests were not run in the complete absence of oxygen. From the averages it will also be seen that light and heat are significant factors.

Photographs of the metal coupons taken after these tests are shown in Appendix C. The photographs are interesting in that the dele-terious effect on the copper and brass are in direct relationship to the percent oxidation shown in Table X. It is also interesting to note that comparison of the coupons in the nitrogen system with those in air show that the metals protected by phosphate i.e., steel and aluminum, are more severely attacked in the nitrogen system. This bears out the obser-vation of Pryor and Cohen (Ref. 19) who found that in the pH range 7.2 - 10.0 sodium phosphate is a much more effective inhibitor when oxygen is

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present than when it is absent. It should be noticed that oxygen is needed not only for the formation of an oxide film, but also to enable the phosphate ions to play their part in blocking the attack at sensitive points where the supply of oxygen is insufficient for the direct formation of oxide. Only if oxygen is available to absorb the electrons over the larger (cathodic) area around these points, will the anodic deposition of HPO_4 = ions at the sensitive points continue and cause the points to become suitably "blocked" or protected.

C. Exposure of Dry MBT to Ultra Violet Light. The analysis of the dry MBT samples exposed to ultra violet showed that very little degradation had taken place and was of the order of 0.9 to 1.0%. The degradation product was found to be chloroform insoluble and was isolated. A potassium bromide pellet was prepared of this product and an infrared spectrum was obtained (Fig. 5). The spectra of all exposed samples can be superimposed. The product was different from that of the oxidation product obtained in solution. It was characterized by bands at 3.0 and 9.0 microns. The 3.0 band was either OH or NH. Because of the sharpness and supporting band at 9.0 microns an NH assignment was made. The 9.0 micron band could be either, phenol, ether and sulfone are ruled out by existing evidence. What may happen is that the MBT tautomirizes and the tautomeric form
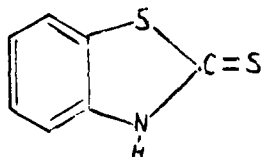
eventually forms a compound of type RSO_2NH_2. The melting points of the degradation products were all comparable and were about that which would be expected of a sulfonamide as follows:

Weatherometer	219°C
Sunlight	216°C.
Ultra Violet Bulb	218°C.
Average	218°C.

It is concluded from above that dry MBT is fairly stable toward ultra violet and that the degradation product in the dry state is different from that found in solution.

D. The chemistry of the above investigation can be explained as follows:

Thiols such as MBT are the sulfur analogs of alcohols. However, oxidation of thiols take a course different from the oxidation of alcohols. This is because the sulfur analog is more easily oxidized than the corresponding oxygen analog, and compounds in which sulfur exists in a higher oxidation state are usually less stable. The strength of S-H bonds

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(83 K Cal) is considerably less than O-H bonds (111 K Cal). We can expect that reactions that are unfavorable with O-H compounds might well be more favorable with the corresponding sulfur compounds. Thus, the oxidation of thiols such as MBT takes place under very mild oxidation conditions to produce disulfides via thioxy radicals.

MBT is a tautomeric substance and exists in two forms (Ref. 15)

thiol form   thione form
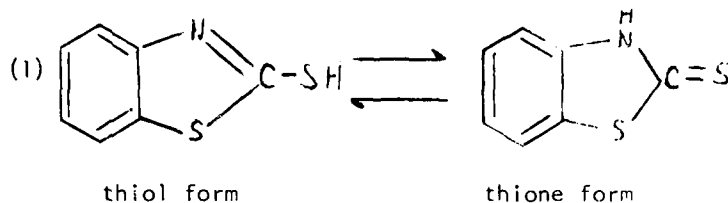
In alcoholic solution i.e. coolant media, MBT exists predominantly in the thione form. In alkaline solution the thione-thiol equilibrium appears to be upset in favor of the "acidic" thiol form (Ref. 16). The oxidation may be represented as follows:
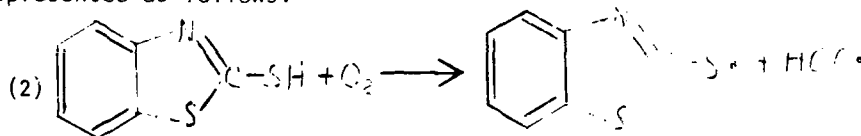
(This reaction is particularly initiated by ultra violet light in the 315 to 325 wavelengths.)

(3) $RSH + HOO \cdot \longrightarrow RS \cdot + H_2O_2$
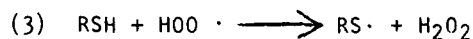
(4) H_2O_2 is unstable especially when heated and decomposes as

follows: $H_2O_2 \longrightarrow 2 \cdot OH$

(5) $R-SH + \cdot OH \longrightarrow H_2O + R-S \cdot$

(6) $2 R-S \cdot \longrightarrow$

benzothiazyl disulfide   (BTD)

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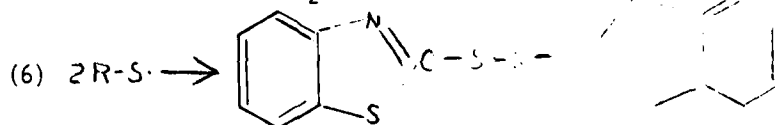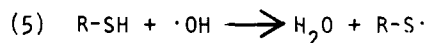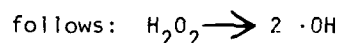
As the above reaction proceeds, the "acidic" thiol form will be consumed, and the equilibrium represented in equation 1 will be continually shifting to the left. The C-S band of the thione form is assigned a wavelength of 6.70 microns and the shifting of the equilibrium can be followed by the diminution of this band.

In gylcol media, the oxidation of MBT to BTD may proceed through a different mechanism, initiated by a molecule induced homolysis of the glycol as shown below:

(7)
$$CH_2 - OH \atop CH_2 - OH \quad +O_2 \longrightarrow \quad \overset{\bullet}{C}HOH \atop CH_2OH \quad + \cdot O\text{-}OH$$
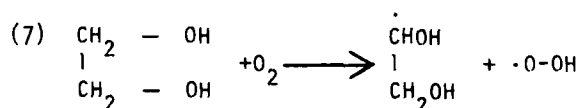
Under varying conditions of temperature, oxygen and light etc. the course of oxidation will vary.

The reactive resultant radical can extract a hydrogen from the MBT producing a free thiyl radical as follows:

(8)

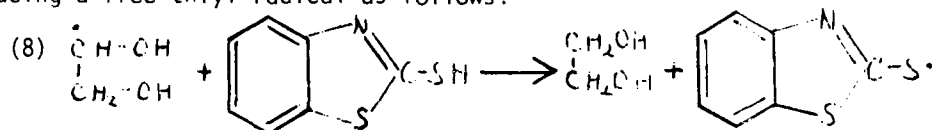The hydrogen abstraction reaction of the thiyl radical shown in (8) is inhibited by the electron, donating groups in the thiol and accordingly the thiyl radical terminates by reaction with a second activated thiyl radical as in (6).

In the absence of air, the glycol is capable of being excited by ultra violet light to a species capable of extracting a hydrogen atom from MBT in a manner similar to the extraction which takes place with secondary butyl alcohol (Ref. 17).

The reversible conversion of disulfides to thiols occurs primarily in enzyme catalyzed activation biochemical reactions which can be represented by:

(9)
$$2\ RS\text{-}H \underset{\text{Reduction activation}}{\overset{\text{Oxidation inactivation}}{\rightleftharpoons}} RS\text{-}SR$$

MBT   BTD
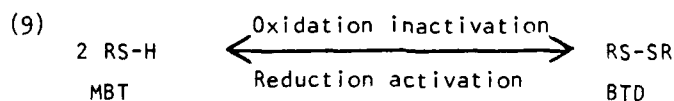
In the system under study however, once the MBT is converted to BTD, it remains in this form. Because of the very limited solubility of BTD the operational implication of excessive amounts of this formation is apparent and musc be considered in antifreeze programs.

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IV. CONCLUSIONS

It has been demonstrated that mercaptobenzothiazole (MBT) is readily oxidized to the terminal molecule of benzothiazyl disulfide (BTD) by way of a free radical mechanism and that this conversion is irreversible in coolant media.

Light, air or a combination of these may be the initiator of a molecule homolysis of the water or glycol which proceeds, depending on the initiator, by different paths to formation of a peroxy or alkoxy radical which subsequently activates the MBT. These reactions are further accelerated by the presence of heat.

BTD is less soluble and therefore more sediment is found in systems where BTD is formed. The possibility of the deleterious operational effect of increased sediment should be considered.

The conversion of MBT to BTD does not adversely effect the corrosion inhibiting effectiveness of the inhibitor system.

V. RECOMMENDATIONS

Since MBT is easily oxidized to BTD which has limited solubility, it is recommended that dosages used in coolant systems be kept to a minimum compatible with inhibiting effectiveness.

VI. ACKNOWLEDGEMENT

The helpful theoretical discussions of Dr. James Sparrow and the assistance of Messrs. Robert G. Jamison and J. P. Doner in obtaining the experimental data is gratefully acknowledged.

VII. REFERENCES

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2. Federal Specification O-A-548a, Antifreeze, Ethylene Glycol, Inhibited, Type I, dated 30 December 1958.

3. Federal Specification O-I-490a, Inhibitor, Corrosion, Liquid Cooling System, dated 26 April 1965.

4. Federal Specification QQ-A-250/4b (2024 Alloy) Aluminum Alloy, Plate and Sheets.

5. Federal Specification QQ-B-613, Brass Leaded and Non Leaded, Plate, Rolled Bar, Sheet and Strip.

6. Federal Specification QQ-C-576, Copper Flat Products (Plate, Bar, Sheet and Strip).

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APPENDIX A

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TABLE I

CORROSION RATING SYSTEM FOR LABORATORY BENCH CORROSION TEST

Rating	Weight Loss (mg./cm^2)
1	0.00-0.10
2	0.2
3	0.3
4	0.4
5	0.5
6	0.6-1.0
7	1.1-3.0
8	3.1-7.0
9	7.1-14.0
10	14.1-50.0
11	50.1 or above
1	any weight gain

To evaluate the corrosion of metal specimens, corrosion ratings were assigned according to the above table based on weight losses per unit area of each specimens, and a collective rating of each set of specimens, i.e., aluminum, copper, solder, steel and cast iron, assigned by totalling the individual ratings. If the metal shows visual corrosion, i.e., pitting, etching, staining, discoloration, the rating is raised by one point. The higher the numerical rating, the greater the corrosion. A rating of 10 or less indicates a satisfactory composition.

TABLE II

GLASSWARE CORROSION TEST (ASTM D-1384)
30% O-A-548a 70% Distilled Water
Painted Glassware

| | With O-I-490a | | | | With BTD Replacing MBT in O-I-490a | | | |
| | Sample A | | Sample B | | Sample C | | Sample D | |
Metal	Visual Inspection	Wt. Loss mg./cm2	Visual Inspection	Wt. Loss mg./cm2	Visual Inspection	Wt. Loss mg./cm2	Visual Inspection	Wt. Loss mg./cm2
Aluminum	Black stain	0.1	Black stain	0.1	Black stain	0.1	Black stain	0.1
Copper	Light stain	0.1	Light stain	0.1	Light stain	0.1	Light stain	0.1
Solder	Light stain	0.2	Light stain	+0.3	Light stain	0.3	Light stain	0.4
Brass	Light stain	0.2	Light stain	0.2	Light stain	0.1	Light stain	0.2
Steel	Light stain	0.1	Light stain	0.1	Light stain	0.1	Light stain	0.1
Cast iron	Light stain	0.1	Light stain	0.1	Light stain	0.1	Light stain	0.1
Rating	8		7		8		10	
pH before	7.9		7.9		7.9		7.9	
pH after	7.9		7.0		8.0		8.2	
RA before	8.9		8.9		8.9		8.9	
RA after	8.0		8.9		7.5		7.3	
gm. sed/100 ml.	0.0148		0.0152		0.0304		0.0242	

RA = Reserve alkalinity.

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TABLE III

GLASSWARE CORROSION TESTS (ASTM D-1384)
MIL-A-11755B - Arctic Antifreeze
Painted Glassware

| | With 0-1-490a | | | | With BTD Replacing MBT in 0-1-490a | | | |
| | Sample A | | Sample B | | Sample C | | Sample D | |
Metal	Visual Inspection	Wt. Loss mg./cm2	Visual Inspection	Wt. Loss mg./cm2	Visual Inspection	Wt. Loss mg./cm2	Visual Inspection	Wt. Loss mg./cm2
Aluminum	Black stain	0.04	Black stain	0.01	Black stain	0.00	Black stain	0.00
Copper	Light stain	+0.01	Light stain	0.00	Light stain	+0.01	Light stain	+0.01
Solder	Light stain	0.00	Light stain	0.00	Light stain	0.09	Light stain	+0.02
Brass	Moderate stain	+0.01	V. light stain	+0.02	Moderate stain	+0.01	Light stain	+0.03
Steel	Black stain	0.04	V. light stain	+0.03	V. light stain	+0.01	V. light stain	0.01
Cast iron	Light stain	+0.07	Light stain	+0.01	Light stain	+0.04	Moderate stain	+0.07
Rating	6		6		6		6	
pH before	7.4		7.4		7.4		7.4	
pH after	8.2		8.2		8.2		8.2	
RA before	9.65		9.65		9.65		9.65	
RA after	5.80		5.80		5.50		6.00	
gm. sed/100 ml.	0.0052		0.0043		0.0175		0.0237	

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TABLE IV

GLASSWARE CORROSION TESTS (ASTM D-1384)
Distilled Water
Painted Glassware

| | With D-1-490a | | | | With BTD Replacing MBT in D-1-490a | | | |
| | Sample A | | Sample B | | Sample C | | Sample D | |
Metal	Visual Inspection	Wt. Loss mg./cm^2	Visual Inspection	Wt. Loss mg./cm^2	Visual Inspection	Wt. Loss mg./cm^2	Visual Inspection	Wt. Loss mg./cm^2
Aluminum	Black stain	0.42	Black stain	0.96	Black stain	0.47	Black stain	1.13
Copper	Heavy stain	0.01	Moderate stain	0.04	Moderate stain	0.02	Moderate stain	0.005
Solder	Moderate stain	0.05	Light stain	0.07	V. Light stain	0.06	V. Light stain	0.14
Brass	Moderate stain	0.03	Light stain	0.02	Light stain	0.04	Moderate stain	0.03
Steel	Light stain	0.04	Light stain	0.04	V. Light stain	0.04	V. Light stain	0.10
Cast iron	Heavy stain	0.29	Heavy stain	0.02	V. Light stain	0.06	Moderate stain	0.01
Rating	9		11		9		12	
pH before	8.9		8.9		8.9		8.9	
pH after	9.1		9.3		9.5		9.5	
RA before	2.3		2.3		2.3		2.3	
RA after	2.3		2.1		2.9		2.3	
gm. sed/100 ml.	0.0065		0.0071		0.0460		0.0367	

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TABLE V

GLASSWARE CORROSION TESTS (ASTM D-1384)
70% Distilled Water 30% O-A-548a
Clear Glass

| | With O-I-490a | | | | With BTD Replacing MBT in O-I-490a | | | |
| | Sample A | | Sample B | | Sample C | | Sample D | |
Metal	Visual Inspection	Wt. Loss mg./cm²	Visual Inspection	Wt. Loss mg./cm²	Visual Inspection	Wt. Loss mg./cm²	Visual Inspection	Wt. Loss mg./cm²
Aluminum	Black stain	0.02	Black stain	0.05	Black stain	0.02	Black stain	0.01
Copper	Moderate stain	0.01	Moderate stain	0.03	Light stain	0.05	Light stain	0.05
Solder	V. Light stain	0.10	V. Light stain	0.10	V. Light stain	0.05	V. Light stain	0.10
Brass	Moderate stain	0.03	Moderate stain	0.07	Light stain	0.07	Light stain	0.03
Steel	Light stain	0.03	Light stain	0.08	Light stain	0.05	Light stain	0.05
Cast Iron	V. Light stain	0.20	V. Light stain	0.01	V. Light stain	0.02	V. Light stain*	0.02
Rating		6		6		6		6
pH before		7.9		7.9		7.9		7.9
pH after		7.8		7.8		7.9		7.9
RA before		8.9		8.9		8.9		8.9
RA after		7.9		7.9		7.9		7.9
gm. sed/100 ml.		0.0102		0.0108		0.0340		0.0373

*Very slight pitting.

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TABLE VI

GLASSWARE CORROSION TESTS (ASTM D-1384)
MIL-A-11755B - Arctic Antifreeze
CLEAR GLASS

| | With 0-I-490a | | | | With BTD Replacing MBT in 0-I-490a | | | |
| | Sample A | | Sample B | | Sample C | | Sample D | |
Metal	Visual Inspection	Wt. Loss mg./cm^2	Visual Inspection	Wt. Loss mg./cm^2	Visual Inspection	Wt. Loss mg./cm^2	Visual Inspection	Wt. Loss mg./cm^2
Aluminum	OK	+0.2	OK, Slight EB	0.01	Slight EB	0.01	Slight EB	+0.01
Copper	Slight tarnish	+0.2	Slight tarnish	0.01	Moderate stain	+0.04	Moderate stain	+0.03
Solder	Slight tarnish	-0.66	Sl. tarnish & P	0.80	Heavy pitting	0.65	Heavy pitting	0.56
Brass	Moderate stain	+0.02	Mod. stain, EB	0.01	Moderate stain	0.01	Moderate stain	+0.03
Steel	EB	+0.01	OK, EB	0.04	OK, EB	0	OK, EB	0
Cast iron	Slight rust, EB	0	Slight rust, EB	0.01	Slight rust, EB	+0.01	Slight rust, EB	0.02
Rating	11		11		11		11	
pH before	7.40		7.40		7.40		7.40	
pH after	7.05		7.10		7.15		7.15	
RA before	14.0		14.0		14.0		14.0	
RA after	14.9		12.9		13.3		13.0	
gm. sed/100 ml.	0.0076		0.0071		0.0320		0.0282	

P = Pitting
EB = Electrolytic burn

TABLE VII

GLASSWARE CORROSION TESTS (ASTM D-1384)
100% Distilled Water
Clear Glass

| | With 0-1-490a | | | | With BTD Replacing MBT in 0-1-490a | | | |
| | Sample A | | Sample B | | Sample C | | Sample D | |
Metal	Visual Inspection	Wt. Loss mg./cm^2	Visual Inspection	Wt. Loss mg./cm^2	Visual Inspection	Wt. Loss mg./cm^2	Visual Inspection	Wt. Loss mg./cm^2
Aluminum	Black stain, EB	0.90	Black stain, EB	0.60	Black stain, EB	0.40	Black stain, EB	0.50
Copper	Moderate stain	+0.06	Moderate stain	+0.02	Moderate stain	+0.005	Moderate stain	+0.01
Solder	OK	0.01	OK	0.01	OK	+0.03	OK	0
Brass	Light stain	+0.05	Light stain	+0.01	Moderate stain	+0.02	Moderate stain	+0.005
Steel	Mod. rust, EB	+0.10	Mod. stain, EB	+0.04	Mod. stain, EB	+0.08	Mod. stain, EB	+0.10
Cast iron	Mod. rust, EB	+0.10	Mod. rust, EB	+0.06	Mod. stain, EB	+0.10	Mod. stain, EB	+0.10
Rating		11		11		9		10
pH before		8.9		8.9		8.9		8.9
pH after		9.2		9.2		9.2		9.2
RA before		2.3		2.3		2.3		2.3
RA after		3.3		3.3		2.8		2.7
gm. sed/100 ml.		0.0022		0.0026		0.0164		0.0217

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TABLE VIII

SUMMARY OF RATINGS (SEE TABLE I)

Glassware Corrosion Tests with Various Coolants
Clear and Painted Beakers (Duplicate Tests)

Coolant	Test	MBT		BTD	
		Clear	Painted	Clear	Painted
30% O-A-548a/70% H_2O	1	6	8	6	8
	2	6	7	6	10
100% H_2O	1	11	9	9	9
	2	111	11	10	12
MIL-A-11755B (Arctic)	1	11	6	11	6
	2	11	6	11	6
Average		9.3	7.8	8.8	8.5

TABLE IX

Glassware Corrosion Tests - Weight of Sediment
(Duplicate Tests)

Coolant	Test	MBT Grams		BTD Grams	
		Clear	Painted	Clear	Painted
30% O-A-548a/70% H_2O	1	0.0102	0.0145	0.0340	0.0304
	2	0.0108	0.0152	0.0370	0.0242
100% H_2O	1	0.0022	0.0065	0.0164	0.0160
	2	0.0026	0.0011	0.217	0.0367
MIL-A-11755B (Arctic)	1	0.0076	0.0052	0.0320	0.0175
	2	0.0075	0.0043	0.0280	0.0237
Average		0.0068	0.0078	0.0281	0.0247

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TABLE X

Comparative Percent Oxidation of MBT to BTD
(By Ultraviolet Absorption Spectrophotometry)

	Air	Nitrogen
Light and Heat (180°F.)	50.4%	27.5%
Dark and Heat (180°F.)	42.4%	26.0%
Light and No Heat (77°F.)	10.5%	5.7%
Dark and No Heat (77°F.)	5.0%	2.2%

Average Air	27.17%
Average Nitrogen	15.47%
Average (Light)	23.5%
Average (Dark)	18.9%
Average (Heat)	38.6%
Average (No Heat)	5.9%

APPENDIX B
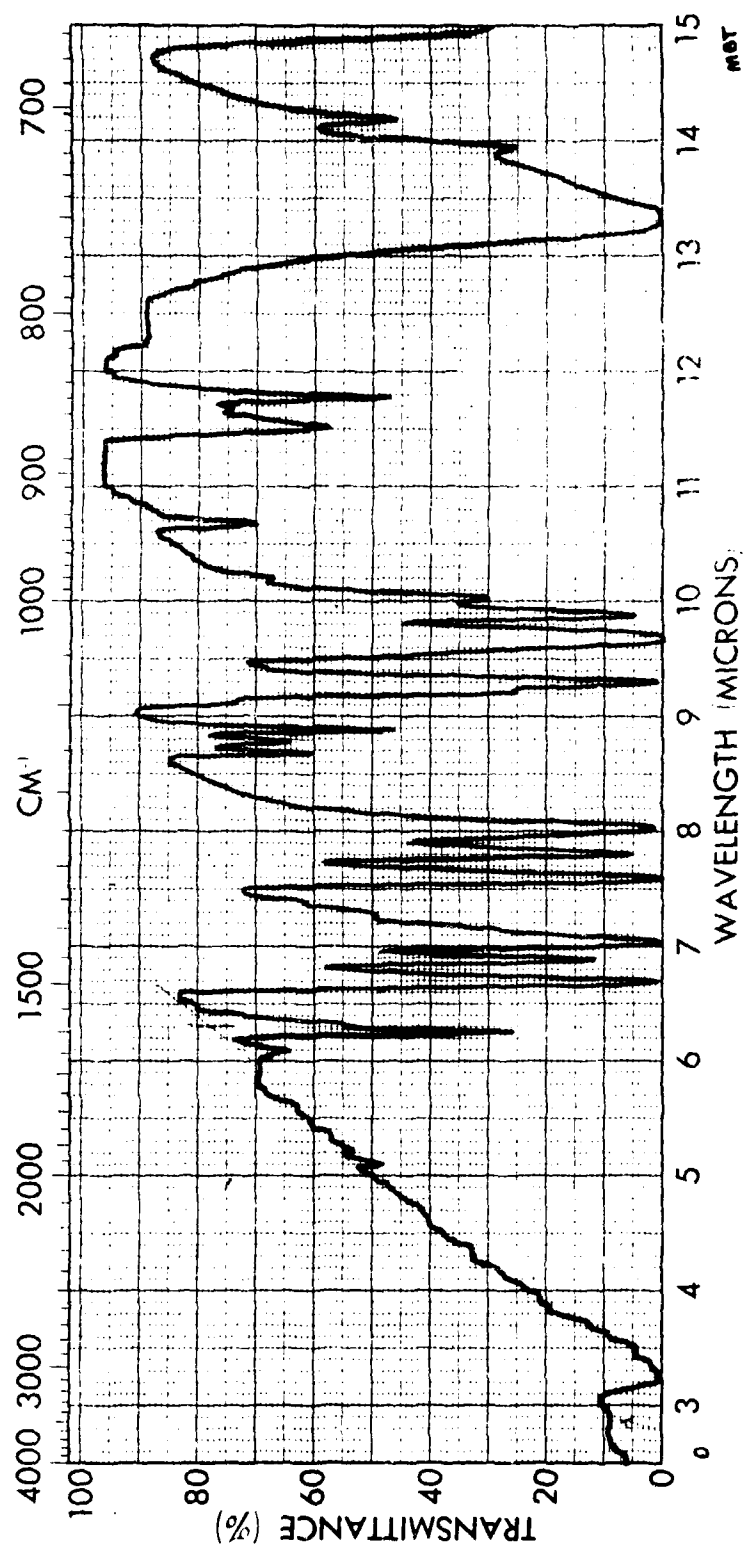
FIGURE I — 2-MERCAPTOBENZOTHIAZOLE
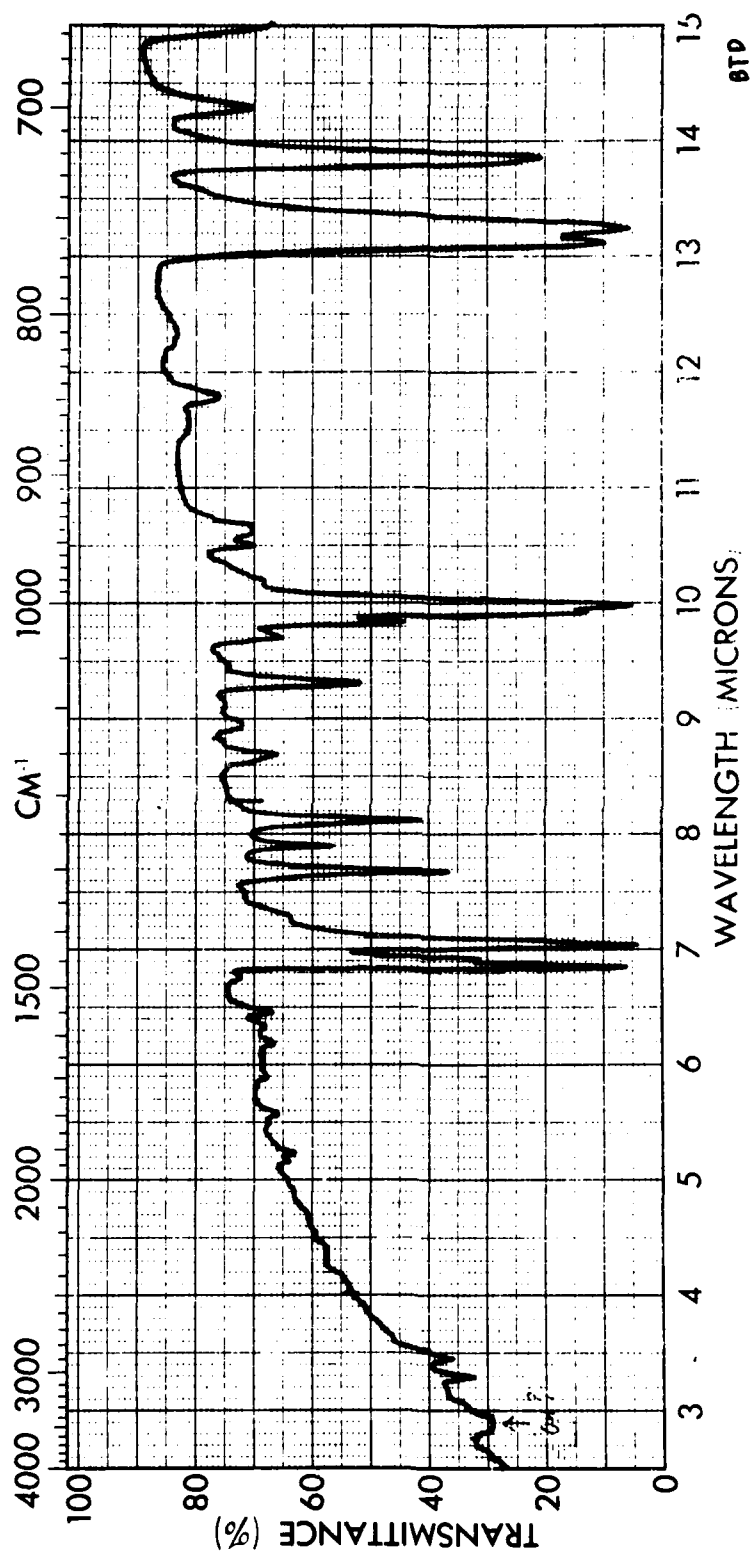
FIGURE 11 - BENZOTHIAZYL DISULFIDE

(Note absence of band at 6.25u)
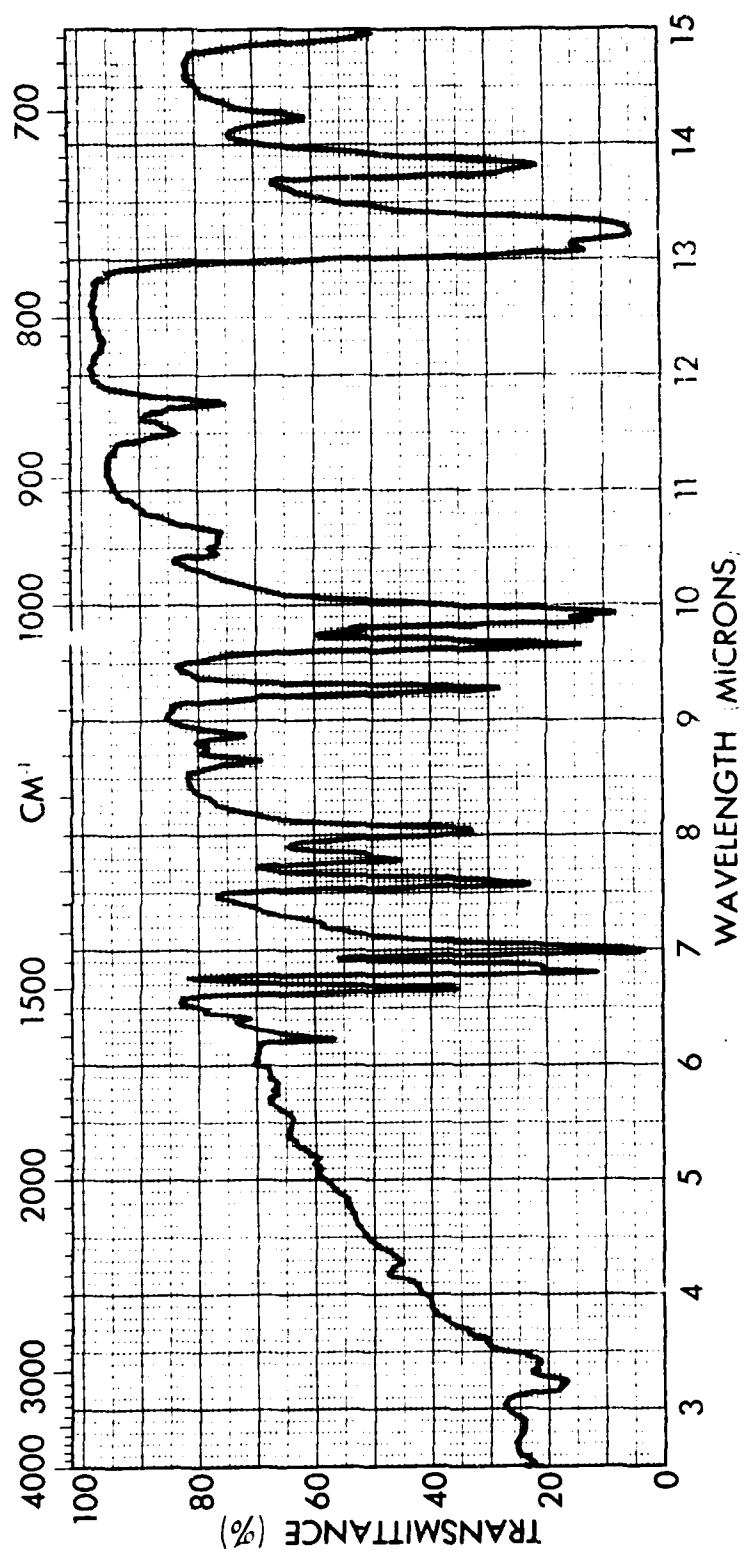
FIGURE III - 25% MBT, 75% BTD

(Note diminishing band at 6.25 u)
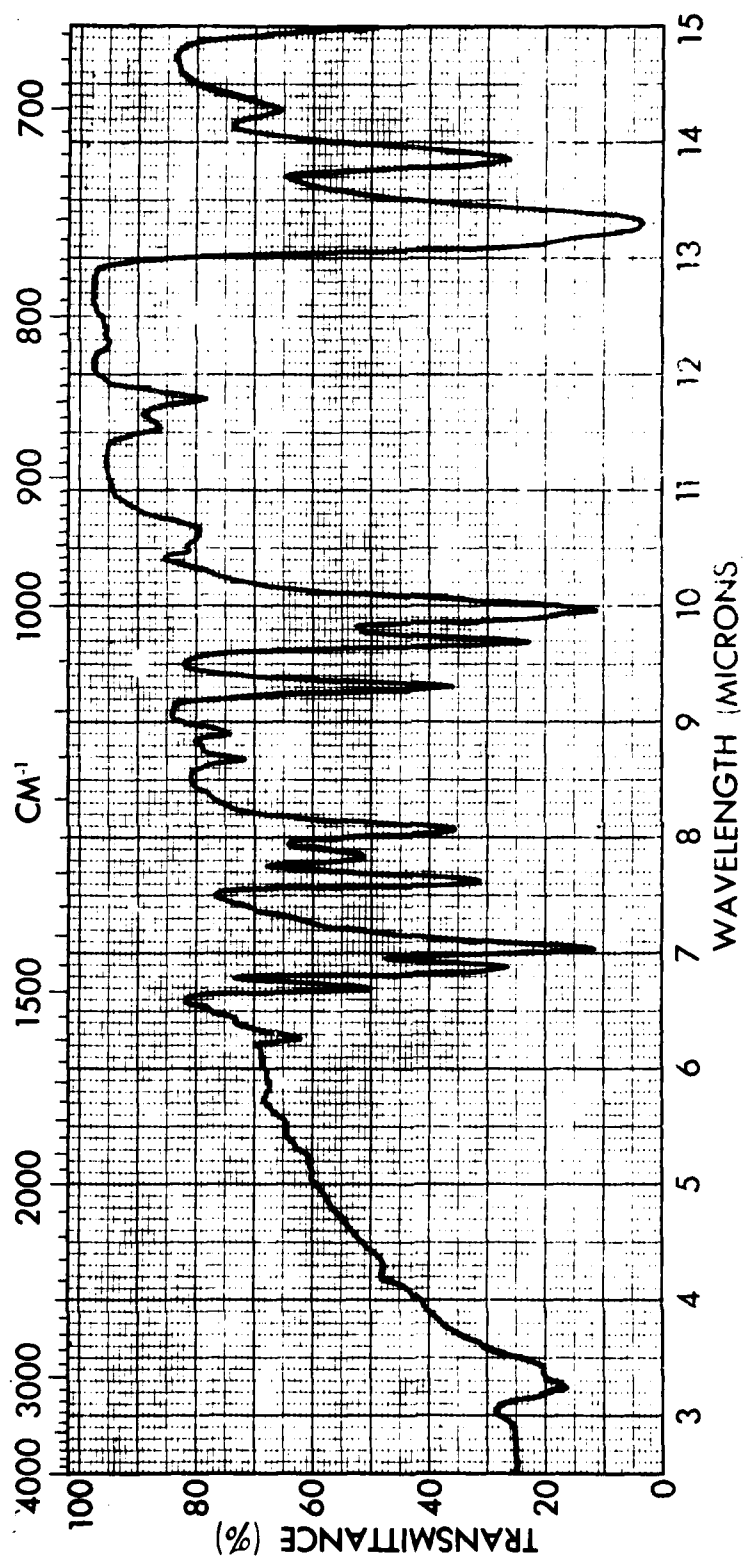
FIGURE IV – 15% MBT, 85% BTD

(Note diminishing band at 6.25u)
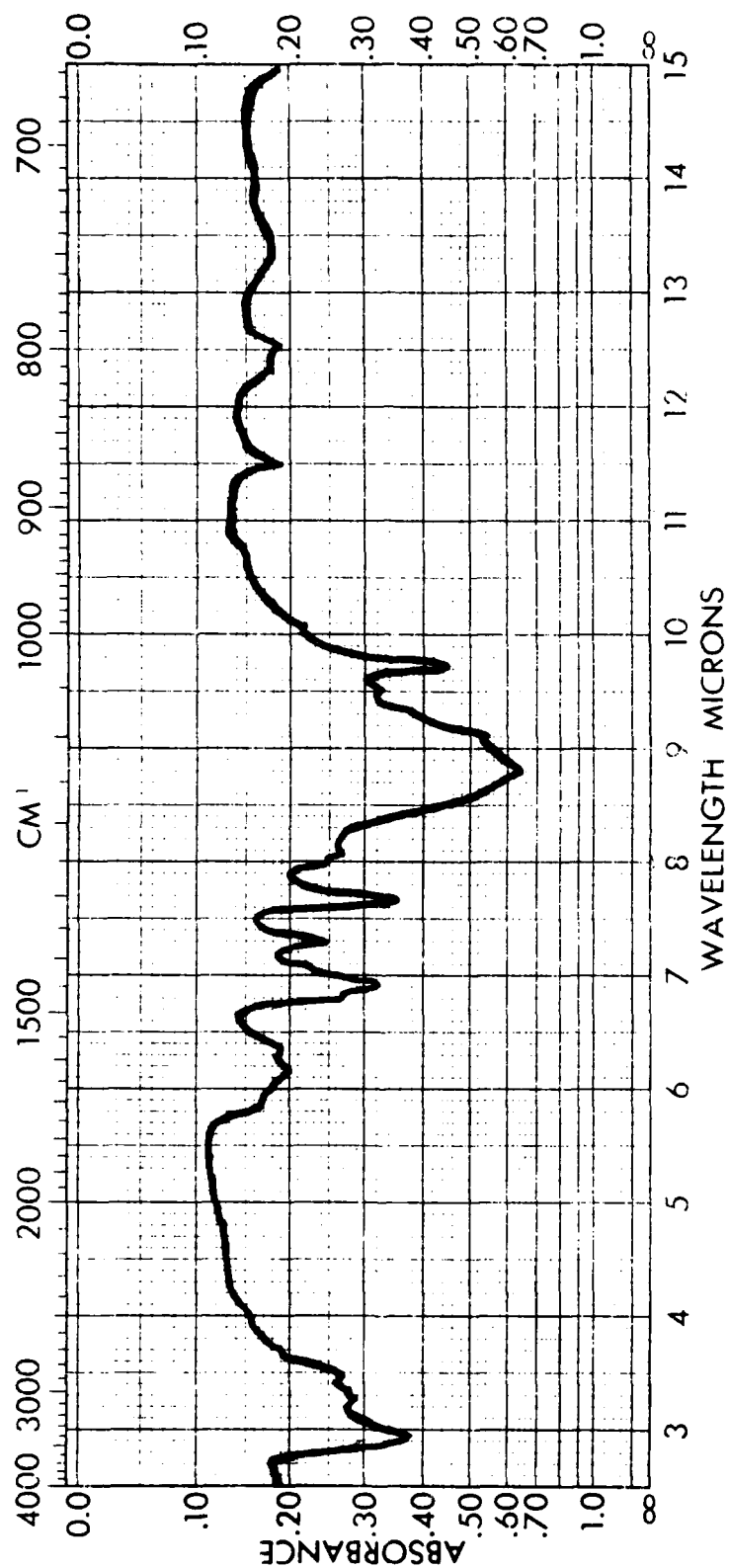
FIGURE V - CHLOROFORM INSOLUBLE PORTION AFTER EXPOSURE OF MBT TO ULTRA VIOLET LIGHT IN WEATHEROMETER.

Fig VI
Working curve for determination of
MBT, BTD composition.

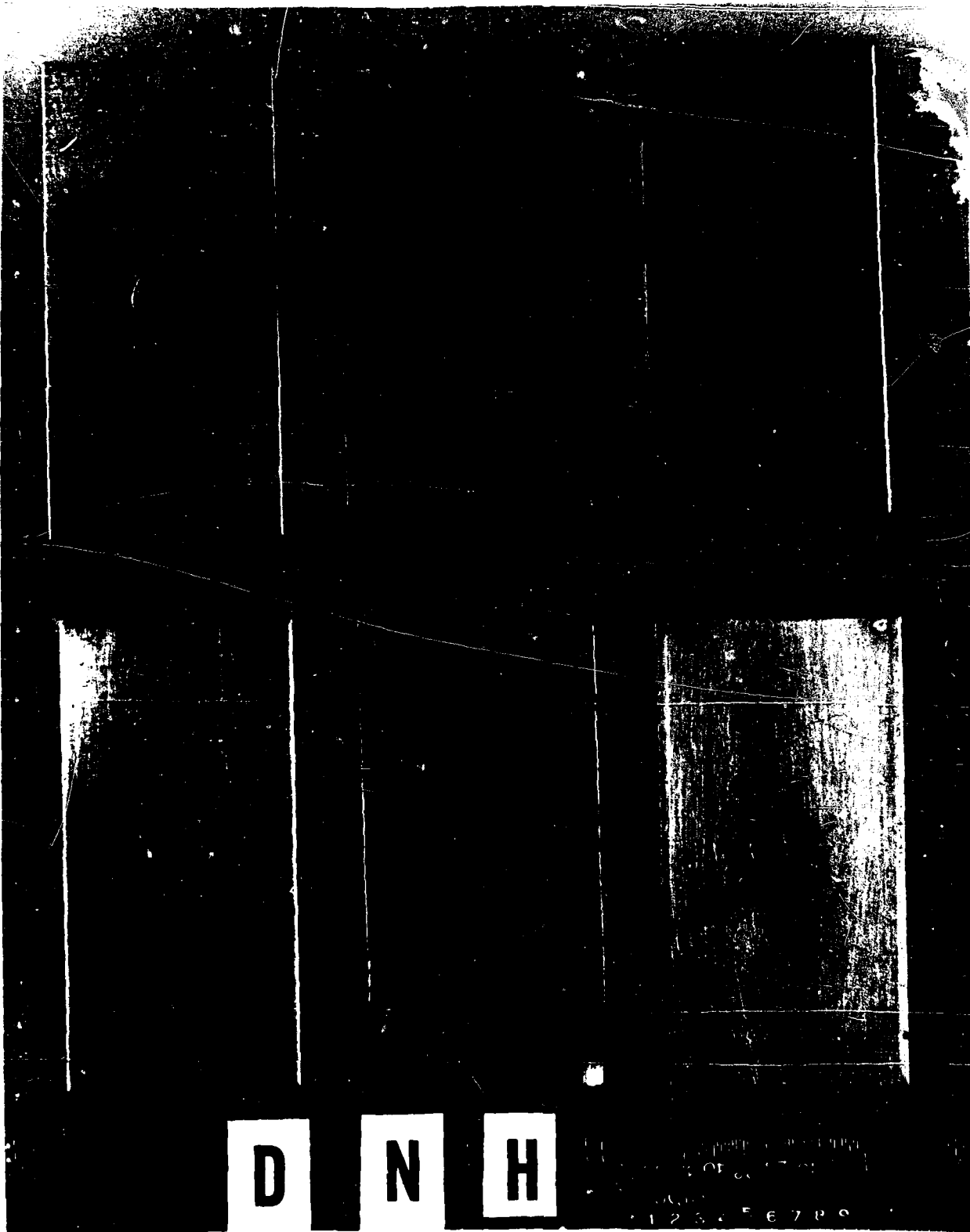"T"

(%MBT)
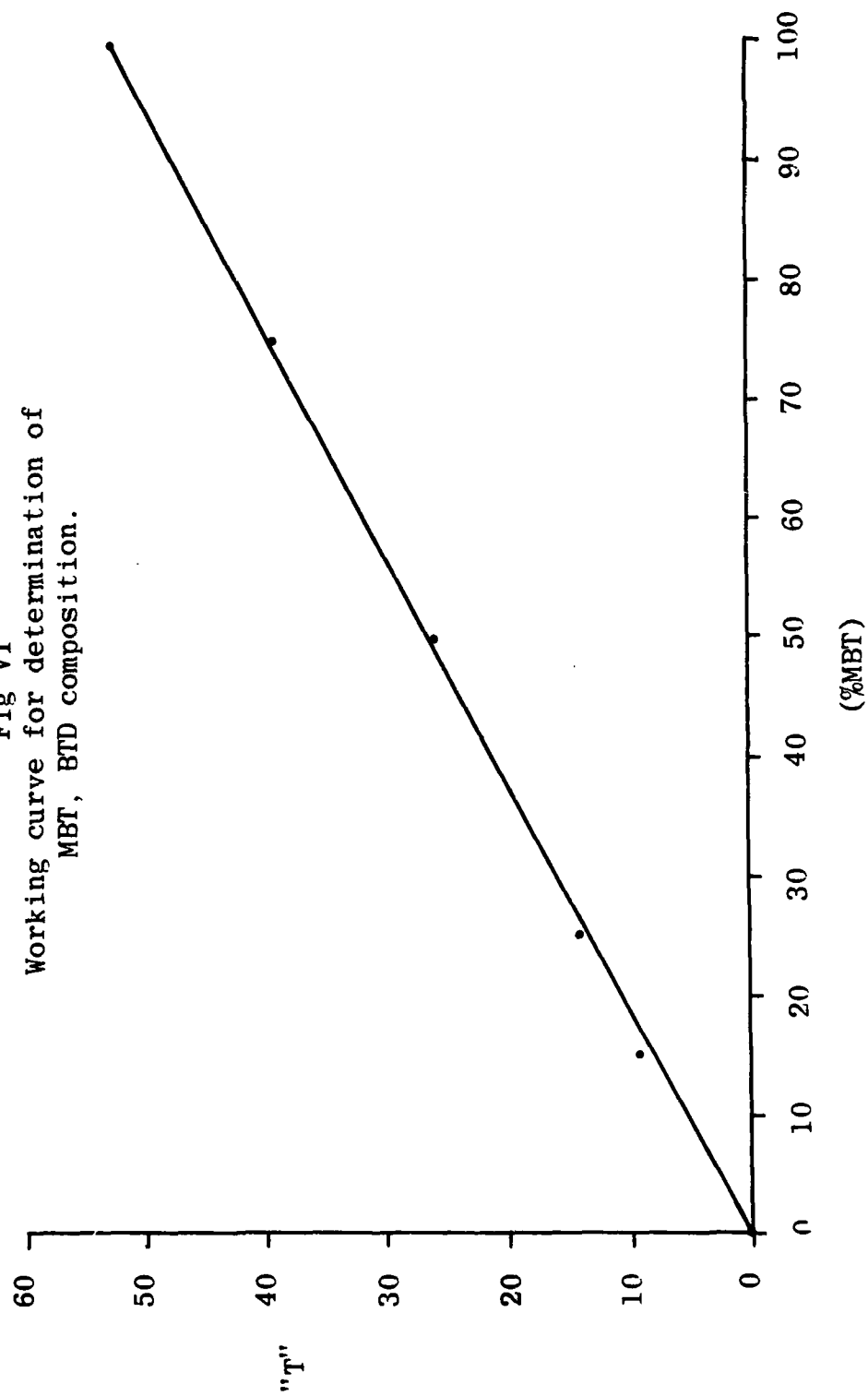
LEGEND

0 = Unexposed, before test

A = Air (100 ml/min.)

N = Nitrogen

L = Light

D = Dark
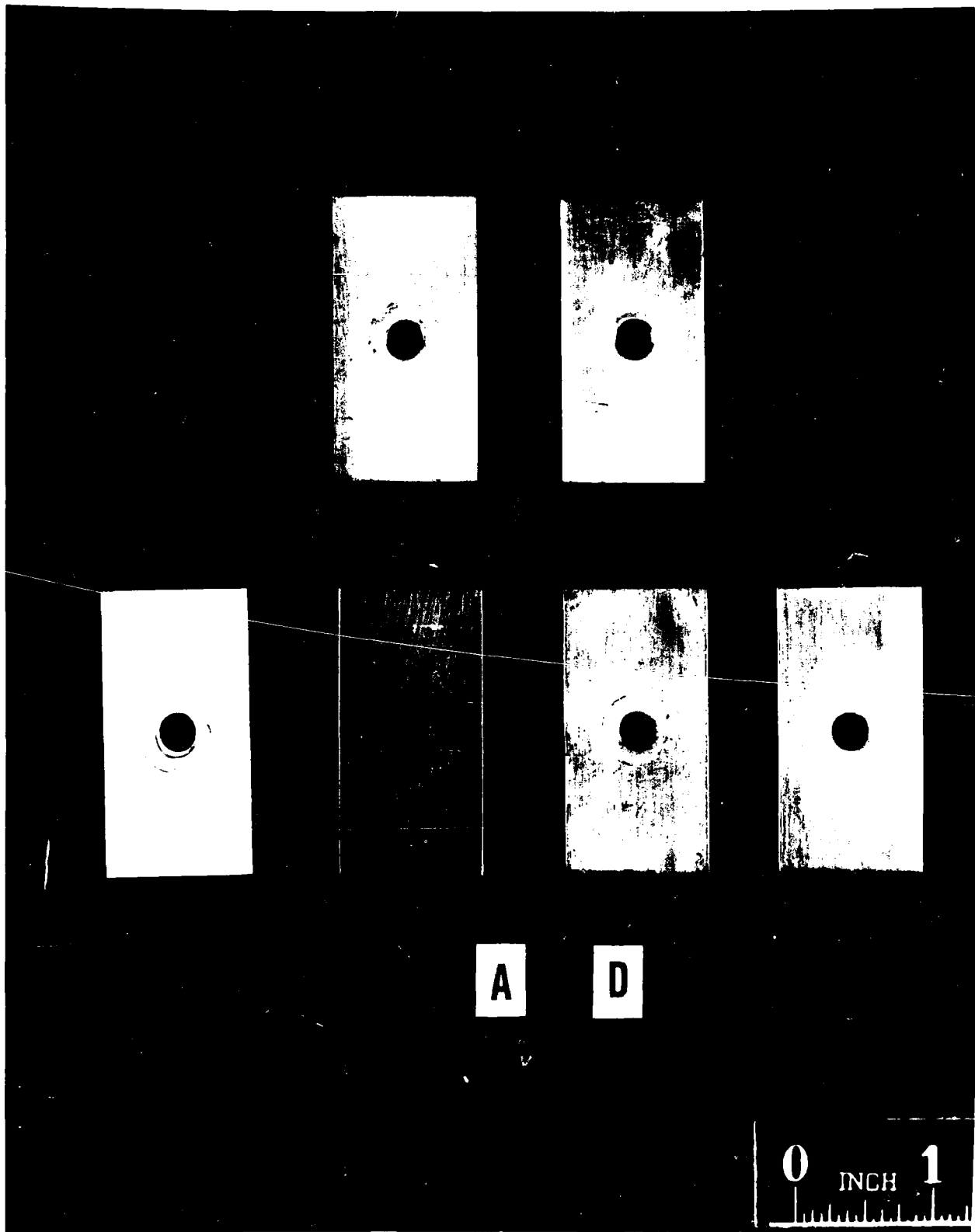
R = Room temperature

H = Heat (180°F.)

DNH

L N H

AHD

A D

0 INCH 1

L D

0 INCH 1